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## Composition of Initiated Cracking Products of High-Sulfur Natural Bitumen

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### Abstract

The analysis of the cracking products of bitumen Karmalskoye deposits (the content of fractions boiling up to 200 °C 6,7 % wt.) has been performed. The influence of power plant coal ash microspheres on orientation of cracking bitumen components is stated. Bitumen cracking leads to significant yields of gas and coke for more than 20 % wt. and destructions of all components. The initiated bitumen cracking in the presence of 10 % microspheres at cracking temperature 450 °C leads to reduction of gas and coke yields and increase in fractions of ibp (initial boiling point) –360 °C at 10 % wt. in comparison with products of the thermal bitumen cracking. The analysis of composition and amount of sulfur compounds in initial bitumen and the cracking products in the various conditions has shown that the thermal cracking leads to increased homologues benzothiophene contents due to partial destruction of resins, and to decrease in the content of homologues dibenzothiophene.

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### 1. Introduction

The decline in reserves growth of low viscosity, the so-called "light" oils in many oil producing regions of the world, including Russia, forms the demand for involvement of unconventional - new refinery hydrocarbon sources, primarily heavy and extra-heavy oil and natural bitumen in the economic turnover<sup>1</sup>. Russia is ranked as the third country after Canada and Venezuela in terms of heavy hydrocarbon reserves. According to various estimates, the reserves of heavy oil in the RF range from 6.3 to 3.4 billion tons. In modern refining industry

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catalytic processes of deep oil processing are widespread, but still they do not provide sufficiently attractive technical and economic performance in the processing of heavy hydrocarbons.

One of the main problems associated with the processing of natural bitumen is the high content of high-molecular compounds - resin and asphaltene molecules, which concentrates most of the heteroatoms present in the feedstock. Amount of resins and asphaltenes defines bitumen properties of both dispersion medium and dispersed phase, as well as natural bitumen aggregate stability of in the thermolysis conditions<sup>2-7</sup>. These compounds have high molecular weight, tend to condense and coke formation during processing, and deactivate catalysts<sup>8-10</sup>. Development of deep destruction methods for heavy oil and natural bitumen to resin-asphaltene components will solve the problem of heavy hydrocarbons refinery and reduce the shortage of hydrocarbon fuels in future.

The purpose of this paper is to identify the main directions of transformation of hydrocarbons and sulphur compounds of the bitumen oils during thermal cracking initiated.

## 2. Experimental

### 2.1 Sample

The object of the study is natural bitumen deposits of the Mordovo-Karmalskoye oil field in Tatarstan.

Table 1 Characteristic of bitumen

Sample	Contents % wt.										
	C	H	N	S	O difference	Oils	Resins	Asphaltenes	ibp–200	200–360	>360
	81.5	11.6	1.1	3.7	2.1	70.3	24.5	5.2	6.7	34.6	58.7

As an additive initiating cracking MS (microspheres) was used, the size of which is 0.2 – 0.4 mm (Table 2). Microspheres were isolated from fly ash produced from coal combustion by the separation processes of hydrodynamic and granulometric classification<sup>11</sup>. The basis of the microsphere chemical composition is formed by iron oxides<sup>11</sup>. In bitumen cracking microspheres were not active, therefore, they had been previously calcined at 800 °C for 120 minutes. The addition of the microspheres was 10 % wt. of the bitumen sample.

Table 2 – Composition of microspheres

Composition, % wt.									
SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	FeO
3.45	1.64	73.39	7.49	0.86	0.22	0.22	0.06	0.16	12.53

### 2.2 Elemental analyses

Elemental analysis of the whole vacuum residues was performed by the microanalytical method using CHNS Vario EL Cube analyzer, O was defined by differences (Table 1).

### 2.3 Fractionation methods

*Material composition.* Group composition of the original oil and cracking products was determined using the traditional pattern: first, the content of asphaltenes was defined in the sample by the Golde's "cold" method. Then, the concentration of resins in produced maltenes was determined by the adsorption method covering the

analyzed product with fumed silica, placing the mixture in the Sokslet's extractor, and successively washing away the components of hydrocarbon (oil) and n-hexane resin with benzene-ethanol 1:1 mixture.

*Liquid adsorption chromatography.* Hydrocarbon type content of oil and cracking products was determined by liquid-adsorption chromatography based on activated aluminum oxide of Grade II Brockmann Activity. A weighed portion of sample was mixed with hexane and uniformly distributed across the surface of the sorbent. Then fraction of saturated, mono- and biaromatic hydrocarbons were isolated with n-hexane, threearomatic hydrocarbons were eluted with hexane – benzene (3:1 by volume), and polyaromatic hydrocarbons – with a mixture of ethanol: benzene (1:1 by volume).

*Gas-liquid chromatography.* The gas-liquid chromatography (GLC) was performed with the chromatograph with quartz capillary column 25 m×0,22 mm, stationary phase SE - 54, gas carrier was helium. When using flame ionization detector for the analysis of the saturated hydrocarbon fractions the linear temperature increase ranged from 80 to 290 °C, programming rate – 15 deg/min, fractions of aromatic hydrocarbons – 2 deg/min.

For the analysis of sulfur compounds, a flame photometric detector was used, the linear increase in temperature ranged from 50 to 290 °C, heating rate of the column – 4 °C/min. Composition of sulfur compounds was determined by comparing the retention times of the individual compounds (de-n-hexylsulfide, benzo thiophene, dibenzo thiophene) and the analyzed components, the data from the literature was also used.

#### 2.4 Method of experiment

The experiments were carried out in an autoclave of 12 cm<sup>3</sup>. Bitumen weight was 7g. Experiments were conducted at temperature 450 °C for 60 – 120 min in the air environment. The mass of the reactor was registered without sample and with sample prepared for thermolysis. After conducting natural bitumen heat treatment the gaseous products yield was determined by weight loss of the reactor with sample after removing gas products from the reactor.

After selection of liquid products the reactor was washed with chloroform and weighed. The resulting difference between the mass of the reactor before and after the experiment was referred as coke.

### 3. Results and discussion

#### 3.1 Features changes cracking products bitumen

It was found that increase in time of bitumen cracking leads to destruction of resinous components. Yield of oils and asphaltenes is reduced by 4.0 % and 0.4 %, respectively, that of gas and coke – by 1.6 %, and increase in the resinous components was 2.8 % wt. at 60-minute process (Table 3). At 100 minutes of cracking destruction of resinous components begins with formation of additional oil components. Increase in the process time up to 120 minutes leads to profound destruction of resins and asphaltenes to form significant amounts of gas and coke. The optimal bitumen cracking time was over 100 minutes - the content of oily components is increased by 3.4 % at a total gas and coke yield by 4 % wt., in this case destruction of high molecular weight components was 24 % relatively.

To increase the depth of destruction of macromolecular components the initiated cracking was conducted. Table 3 shows the composition of the bitumen cracking products in the presence of MS. Cracking in the presence of microspheres (duration was 60 minutes) increases the oil yield by 4.9 % due to the processes of resin destruction (content decreases by 7.7 % wt.). By increasing the time the initiated bitumen cracking up to 120 minutes the reduction of the asphaltenes and resins occurs in liquid cracking products by 10.6 % and 0.7 % wt., respectively, as compared to the initial sample. Oils yield increased by 7.3 % with low overall coke and gas yield (totally 4 % wt.). It can be concluded that the introduction of MS leads to slower reactions of gas and coke formation.

Table 3 – Bitumen and initial cracking product material balance and composition under different conditions

Cracking conditions	Content, %wt.			Liquid products, % wt.		
	Gas	Liquid	Coke	Oils	Resins	Asphaltenes
Bitumen	0	100	0	70.3	24.5	5.2
cracking : 60 min	0.6	98.4	1.0	66.3	27.3	4.8
100 min	1.8	96.2	2.0	73.7	17.1	5.4
120 min	14.2	79.6	6.2	65.4	11.6	2.6
+ MS: 60 min	1.0	97.1	1.9	75.2	16.8	5.1
100 min	1.4	96.4	2.2	76.3	15.0	5.1
120 min	1.5	96.0	2.5	77.6	13.9	4.5

### 3.2 Oils natural bitumen and its cracking products composition analysis of the of under different conditions

In the initial bitumen oils monoaromatic compounds 24.1 % predominate, about the same amount of bi - and threearomatic components (17.6 and 17.2 %, respectively), the lowest content in saturated and polyaromatic - 5.4 and 6.0 % wt. (Table 5).

At cracking of bitumen for 60 minutes the oils content decreases by 4.1 % wt., probably, due to condensation reactions of oil components. Decrease in the content of three- and polyaromatics compounds is observed by 6.7 and 1.4 %, respectively, which are partially condensed to form resinous components. Increase in the content of mono- and biaromatic components 2.7 and 4.1 % wt., respectively, takes place. Bitumen cracking for 60 minutes leads to decrease of saturated components by 2.8 % wt. due to destruction and cyclization reactions.

Table 5 – Oils group composition of bitumen after cracking under different conditions

Cracking conditions	% wt. oils	$\rho$ oils g/cm <sup>3</sup>	Content, % wt.				
			saturated	monoaromatic	biaromatic	threearomatic	polyaromatic
Bitumen	70.3	0.9065	5.4	24.1	17.6	17.2	6.0
cracking : 60 min	66.2	0.9015	2.6	26.8	21.7	10.5	4.6
120 min	65.2	0.9063	4.0	24.2	14.7	12.3	10.0
+ MS: 60 min	75.2	0.9107	2.7	34.8	28.7	5.2	3.8
120 min	77.6	0.9114	5.0	28.2	24.2	8.8	11.5

Increase in the cracking duration up to 120 min leads to reduction in the oil yield by 5.1% in comparison with the initial bitumen and by 1.0 % wt. as compared to the cracking over 60 min. In these experimental conditions there observed the profound destruction of resins and bitumen oil components, the saturated components content increases by 1.4 % wt. as compared to the thermal cracking for 60 min. Due to deeper destruction of resinous components the increase in three- and polyaromatic compounds by 1.8 and 5.4 % wt. is observed. In comparison with the composition of the original bitumen the content is three aromatic reduces by 4.9 % and poly- increases by 4 % wt.

Bitumen cracking in the presence of microspheres (10 % wt., 60 min) increases the oil content by 4.9 % wt. and their density (up to 0.9107 g/cm<sup>3</sup>). Content of saturated compounds decreases to 2.7%. Also the output of

mono- and beiaromatic components increases by 10.7 and 10.1 % wt., respectively. Partial destruction of three- and polyaromatic compounds occurs, their content reduces by 12.0 % and 2.2 % wt., respectively.

Increase in initiated cracking duration to 120 min in the presence of the microspheres results in increasing amounts of oil of 7.3 % by weight (2.4 % wt. as compared to initiated cracking within 60 minutes), the oil density increased to 0.9114 g/cm<sup>3</sup>. Patterns of change in oil composition during the initiated cracking are similar to those of thermal cracking. The saturated compounds reduce to 5.0 % wt. The yield of mono- and biaromatic components increases by 4.1 and 6.6 % (less than 6.6 and 3.5% in comparison with the products of initiated cracking within 60 min). Due to the deeper destruction of resins content of polyaromatic components increases by 5.5 % (11.5 % wt). Under these cracking conditions content of threearomatic components amounts 8.8 %, which is 8.4 % less than the original bitumen and 3.6 % wt. more than cracking with microspheres for 60 min.

### 3.3. Composition of sulfur-containing components of the original oils and bitumen cracking products

Analysis of the chromatographic oil fractions of bitumen showed that sulfur compounds are generally represented by homologues (C<sub>3</sub>-, C<sub>4</sub>-, C<sub>5</sub>-) BT (benzothiophene), and (C<sub>2</sub>-, C<sub>3</sub>-) DBT (dibenzothiophene).

Thermal effects on bitumen result in the formation of homologues C<sub>1</sub>BT absent in composition of base oils. With the increase in duration of thermal cracking the content of these compounds increases 10 times. Bitumen cracking over 60 min results in an increase in the content of compounds C<sub>2</sub>BT 5.5 times. Longer thermal cracking contributes to the significant increase in the content of homologues C<sub>2</sub>BT, probably, due to redistribution of sulfur-containing fragments of resin cracking products (increase 20.3 times).

Content of C<sub>3</sub>BT homologues increases 3.5 times under bitumen heating for 60 minutes and remains at this level during thermal cracking for 120 min. The content of homologues reduces (C<sub>4</sub>+C<sub>5</sub>)BT 2.2 - 22.6 times (duration thermocracking 60 and 120 min, respectively). Under bitumen heating for 60 minutes a slight increase in the content of dibenzothiophene is observed. Increase in duration of thermal cracking leads to the reduction of the content of the compound 21.4 times. Thermal bitumen cracking for 60 minutes leads to reduction of the content of dibenzothiophene C<sub>1</sub>DBT homologues C<sub>2</sub>DBT and C<sub>3</sub>DBT, increase in the duration of the thermal exposure to 120 min promotes deeper degradation of compounds of this group, a decrease in the contents 21.9, 62.3 and 89.1 times, respectively, is observed, which is probably due to condensation reactions of DBT homologues in “resins → asphaltenes → coke” pattern.

Composition of sulfur compounds of the liquid cracking products in the presence of MS differs from the thermal cracking products. In the products of initiated bitumen cracking (duration 60 min) the formation of homologues C<sub>1</sub>BT is also observed, their content does not change with increasing duration of the process. Cracking in the presence of the microspheres for 60 min results in the formation of homologues C<sub>2</sub>BT (contents increases 10.8 times). Increase in the duration of the process (120 min) does not affect the content of these compounds.

Table 6 Composition of sulfur group compounds oils cracking bitumen under different conditions

Cracking conditions	Content of sulfur compounds, % wt.							
	C <sub>1</sub> BT	C <sub>2</sub> BT	C <sub>3</sub> BT	(C <sub>4</sub> +C <sub>5</sub> )BT	DBT	C <sub>1</sub> DBT	C <sub>2</sub> DBT	C <sub>3</sub> DBT
Bitumen	-	0.0634	2.3177	3.8567	0.3088	1.0067	2.2671	2.4500
cracking : 60 min	0.0328	0.3503	8.0036	1.7291	0.3381	0.6386	0.9242	0.2521
120 min	0.3140	1.2869	8.0944	0.1707	0.0144	0.0458	0.0364	0.0275
+ MS: 60 min	0.1207	0.6845	11.3443	1.4328	0.1679	0.0687	0.0676	0.0586
120 min	0.1235	0.6389	8.9936	2.0352	0.1087	0.2011	0.3001	0.1095

The bitumen cracking in the presence MS leads to C<sub>3</sub>BT homologues formation (content increases 4.9 times). Increase in initiated cracking promotes partial destruction of the compounds formed. Degradation of (C<sub>4</sub> + C<sub>5</sub>)BT homologues (cracking initiated within 60 min) is observed in 2.7 times, longer exposure to heat up to 120 min promotes the formation of compounds of this group (content increases 1.4 times).

DBT content in the bitumen cracking products in the presence of the MS decreases to 1.8 - 2.8 times (duration is 60 and 120 min, respectively). Amount of dibenzothiophene derivatives reduces (initiated cracking is 60 minutes), increase in the process duration leads to the increase in content of DBT homologues 2.9 4.4 and 1.9 times, respectively, which is probably due to deep thermal degradation of resinous-asphaltene components and the ingress of sulfur fragments in oils.

#### 4. Conclusions

It has been shown that bitumen cracking reduces oil content in the liquid cracking products by 4.9 % and sulphur 0.79 % wt. Initiated bitumen cracking leads to an increase in the oil content of the liquid cracking products by 7.3 %, the sulfur content decreases by 0.36 % wt.

Analysis of oil in bitumen and cracking products in different conditions showed significant differences in the composition and content of benzothiophene and dibenzothiophene homologues. It was found that at bitumen cracking the content of benzothiophene homologues increases, which is probably due to sulfur-containing fragments of resins entering the composition of oils. Increase in time of cracking leads to significant decrease in the content of DBT homologues, which is probably due to condensation reactions of DBT homologues of the “resins → asphaltenes → coke” pattern.

In the composition of liquid product oils of cracking with the addition of microspheres the total content of BT homologues is more than that of cracking. Increase in time of initiated cracking leads to greater destruction of BT homologues as compared to that of thermal cracking. Initiated cracking (duration 60 min) results in profound destruction of DBT homologues (6-fold as compared to thermal cracking). It is found that increasing the duration of initiated cracking up to 120 min leads to deeper destruction of resin-asphaltene components, sulfur fragments of which enter the oil increasing the content of DBT homologues.

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